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14. ABSTRACT
The galvanic interaction of coated AA7075-T6 panels with stainless steel fasteners during immersion in NaCl solution and in a salt spray chamber was studied. Galvanic current and optical profilometry were used to determine the extent and morphology of attack. Coatings were compromised at the fastener hole due to mechanical damage from the fastener and inadequate coating coverage. EIS was used to determine the extent of coating protection at the fastener hole and compare various fastener hole configurations with the protection away from the fastener hole. Impressed current was used to control of the amount of charge passed, as well as the rate at which it is passed.

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Corrosion Degradation of Coated Aluminum Alloy Systems through Galvanic Interactions

ONR Grant # N00014-13-1-0738

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Abstract:

Structural aluminum alloys are used in aircraft because of their low density and relatively high strength. While exhibiting significant general corrosion resistance, these alloys are susceptible to various forms of localized corrosion, such as pitting, intergranular corrosion, etc. When in galvanic contact with fasteners noble to the aluminum alloy panel, these phenomena can be much more aggressive. In an effort to mitigate these problems, multi-layer coating systems are utilized by blocking the aluminum alloy from aggressive environments and preventing galvanic contact with dissimilar metals. However, defects in these coatings may exist from the time of their application or they may form over time, thereby leading to galvanic interaction with the fastener and localized attack of the underlying panel. In addition, delamination of coating at these sites can result in accelerated attack as the environment becomes more aggressive in the shielded delamination areas.

Initial work for this project focused on the galvanic interaction of aluminum alloy 7075-T6 panels with stainless steel 316 fasteners when coated with either a chromated (chromate conversion coating, chromate-rich primer) or non-chromated (adhesion promoting pretreatment, praseodymium-rich primer) system in two environments: immersion in five weight percent sodium chloride and a continuous fog salt spray chamber. A test panel configuration using a scribed Al alloy panel and isolated fasteners was used. Galvanic current data can be acquired during exposure to determine total charge passed due to galvanic interaction between the fastener and panel for the purpose of approximating the extent of aluminum dissolution and comparison of the two coating systems. Post-exposure optical profilometry has been conducted on samples to gain insight on the morphology of the attack, as well as to quantify the corroded volume of material. Analyses of this galvanic current data and morphology have been coupled to survey what coating strategy could be more beneficial.

Additional work focused on identifying the susceptibility of certain areas of the test panel to localized attack and development of a damage function for galvanic corrosion degradation in coated aluminum alloy systems. Coating performance can be compromised at the fastener hole due to mechanical damage from the fastener and from inadequate coating coverage. Electrochemical impedance spectroscopy (EIS) has been utilized to determine the extent of coating protection at the fastener hole and assess the effects of defects that may serve as initiation sites for accelerated attack. Various fastener hole conditions have been compared to the protection afforded by the coating in areas away from the fastener hole. Impressed current has also been used to determine the feasibility of attack

initiating when the unintentional coating defects within the fastener hole are not a factor. This process involves current being passed from a counter electrode to a panel without fasteners in solution, allowing control of the amount of charge passed, as well as the rate at which it is passed. With the absence of fasteners, current may be passed to any defect, regardless of proximity to the fastener hole.

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Introduction:

The low density, high strength, and general corrosion resistance of aluminum alloys make them a common material in use for many structural applications, including on naval aircraft, which can be subjected to aggressive environments such as carrier flight decks. Unfortunately, these alloys are susceptible to localized corrosion in the form of pitting, intergranular corrosion, cracking, and exfoliation, and they must be protected by the application of a coating system to block the environment and provide inhibiting action. The corrosion attack on aluminum alloy panels can be accelerated greatly by a galvanic driving force when they are connected by, and thus electrically coupled to, noble metal fasteners. Corrosion caused 22.4% of the non-available days for all USN/USMC aircraft in FY 2009, which is the single largest operational cost and readiness degrader[1]. Furthermore, 80% of cracks in Navy aircraft initiate at corrosion pits, and 70-95% of the initiation sites are galvanic interfaces[2]. This perspective indicates that it is critical to understand, mitigate and prevent galvanic corrosion of the sort that is common on Navy aircraft. There is a strong desire in the Navy to change the aircraft design paradigm by incorporating corrosion into the design process, and to have a predictive model for corrosion degradation that can inform maintenance decisions.

The rate of corrosion degradation of an aircraft component will depend on the materials of construction, protective measures such as coatings and cathodic protection, defects introduced into the protection system during manufacture and lifetime service, design considerations such as galvanic interactions and crevices, and finally the details of the exposure environment, including but not limited to time of wetness, chloride deposition, pH, temperature, and local environment concentration. This complex system provides a challenge for the development of a useful tool for corrosion design guidance and prediction of lifetime or required service intervals.

Recent advances have resulted in commercially available software programs that are powerful tools for corrosion prediction. For example, the GalvanicMaster program from Elsyca uses a finite element framework with non-linear boundary conditions for the electrochemical reactions and accounts for mass transport and the IR drop in the electrolyte based on a thin film approximation for the environment. However, these programs still provide relatively simplistic descriptions of the complex system detailed above, and there is need for further improvement if these programs are to be of real use. For example, they do not handle localized corrosion in a sophisticated manner. Improvements will require a deeper

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1 Bill Nickerson, ONR SBA Structures and Materials Informational Meeting, 9/13/12

2 Bill Nickerson, workshop in California, MD, 7/25/14

3 Bill Nickerson, workshop in California, MD, 7/25/14

3 Matzdorf, C.A., W.D. Nickerson, B.C. Rincon Troconis, G.S. Frankel, Longfei Li, and R.G. Buchheit. "Galvanic Test Panels

understanding of the initiation and growth of various forms of localized corrosion under conditions of relevance to airframes, i.e. attack at defects in coating systems with galvanic interactions in a changing atmospheric environment.

Objective:

The goal of this project was to study the mechanism of coating degradation and the initiation of localized corrosion during galvanic coupling of high strength Al with a noble metal fastener. Both coating degradation and localized corrosion initiation are critical steps in the failure process that must be handled appropriately by corrosion-design and failure-prediction programs. Previous work has shown the utility of galvanic current measurements and optical profilometry analysis for the assessment of corrosion damage resulting from galvanic interaction of aluminum alloy substrates and stainless steel fasteners in the presence of an intentional extrinsic coating defect, such as a scribe. The goals of this work were as follows:

1. Assess the extent and morphology of degradation through galvanic interactions between coated AA 7075-T6 panels and stainless steel fasteners in the absence of an intentional defect.
2. Determine attack initiation sites and evaluate how coating condition may impact degradation, particularly in the vicinity of fastener through-holes.
3. Examine the use of impressed anodic current as an accelerated corrosion test to mimic the effect of galvanic interactions with reduced testing time and manual control of current.

Approach:

A galvanic test panel designed by NAVAIR engineers[3] was used to accelerate corrosion degradation during testing and to evaluate the real situation of galvanically-accelerated attack. The test panel configuration includes a coated Al alloy plate containing 4 holes, through which fasteners are attached, Figure 1a. In the standard NAVAIR approach, scribes are created in the coating beneath two or more of the fasteners as shown in Fig. 1a. In this work, the fasteners were isolated from the Al alloy panel, but then connected through a zero-resistance ammeter (ZRA) by wires, Figure 1b. The whole assembly is embedded in an epoxy puck to cover the backside of the panels and the wire connections. This approach allows measurement of the galvanic current flowing from each of the fasteners, or combinations of fasteners. The sample can be immersed in a corrosive fluid, or exposed to a corrosive atmosphere such as a salt spray chamber or seaside beach exposure. The connecting wires are long enough to extend to the outside of a salt spray chamber. The quantification given by the galvanic current provides enhanced understanding of the rates and extents of galvanic interaction, and these measurements can be made in situ in real time during the attack. Optical profilometry (OP) was also used to make quantitative assessments of the extent of damage after removal from the corrosive environment. OP provides a topographic map of the corroded surface with excellent resolution. It is not electrochemical in nature and requires no ZRA, so it is not a real time measurement.

The performance of both a chromated and non-chromated coating system on AA 7075-T6 panels was studied. Unlike previous work, the test panels contained no intentional defect such as a scribe. This allows the study of the initiation of attack, not just the propagation of attack. The aggressive environments include immersion in chloride solution and the salt spray conditions of ASTM B117. The

[3] Matzdorf, C.A., W.D. Nickerson, B.C. Rincon Troconis, G.S. Frankel, Longfei Li, and R.G. Buchheit. "Galvanic Test Panels for Accelerated Corrosion Testing of Coated Al Alloys: Part 1—Concept." *Corrosion* 69.12 (2013): 1240-246.

non-chromated system consisted of Prekote adhesion-promoting surface pretreatment, a praseodymium-rich primer, and a polyurethane topcoat. The chromated system included a chromate conversion coating (CCC) pretreatment, a chromate-rich primer, and the same polyurethane topcoat. Previous work has shown that trivalent chromium process (TCP) treated samples behave similarly to CCC-treated samples and that untreated samples or samples coated with non-chromium pretreatment (NCP) behave similarly to those with an adhesion promoter[4]. Corrosion resistant (CRES) SS316 fasteners were attached to all panels as the source of galvanic interaction for the aluminum alloy panel. Characterization was performed using the same methods described above: galvanic current measurements using a ZRA and topographic assessment by OP.

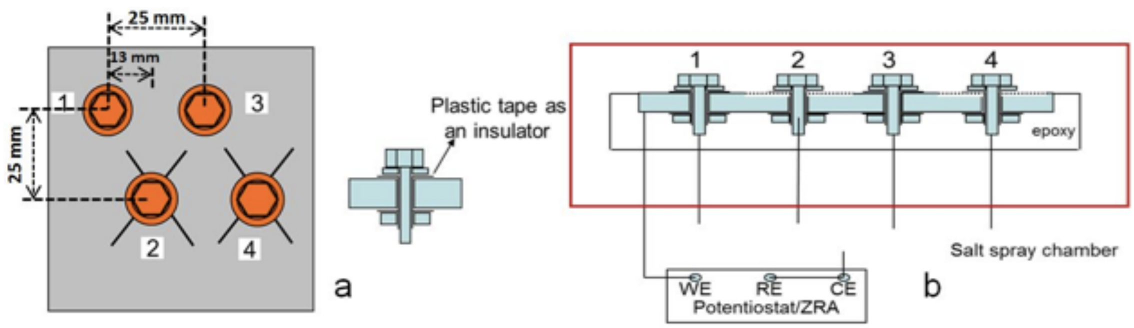


Figure 1: Schematic representation of a) NAVAIR test panel, b) OSU modification. The red box represents a salt spray chamber, but the exposure can be in any corrosive environment. Note that the scribes shown in a) are not used in this work.

Abbreviations List:

AA – Aluminum Alloy
CCC – Chromate Conversion Coating
EIS – Electrochemical Impedence Spectroscopy
NCP – Non-chromium Pretreatment
OP – Optical Profilometer
TCP – Trivalent Chromium Process
CRES – Corrosion Resistant Stainless Steel
ZRA – Zero Resistance Ammeter

Results and Discussion:

Galvanic Interaction:

Coated panels prepared as described above were provided by NAVAIR personnel in Patuxent River, MD. CRES fasteners and wires were attached, and the assembly was mounted in epoxy as shown in Figure 1b. Again, scribes were not created in the panels. The fastener and panel wires were all connected together during the entire period of exposure except for intermittent measurements of galvanic current during which time the panel wire was connected to one side of the ZRA the fastener wires were all connected to the other side.

The galvanic current measured for the two coating systems during exposure to ASTM B117 and for the non-chromated system immersed in 5% NaCl are sorted by color in Figure 2. The different symbol types for each color represent data from replicate experiments. A general trend is observed for both coating

[4] Zhicao Feng, Joshua Boerstler, G. S. Frankel, and C.A. Matzdorf, "Effect of Surface Pretreatment on Galvanic Attack of Coated Al Alloy Panels," *Corrosion*, **71** (2015) 771-783.

systems in salt spray exposure. During the initial period of exposure, approximately 300 h, the current increased approximately linearly with time for all coating systems. After this period, the current tended to reach a plateau, and then remain relatively constant with further exposure time. The plateau galvanic current for the chromated coating system was consistently lower than that for the non-chromated system. Integration of the current over time provides a measure of the total charge passed, and average values of 374 and 498 C were found for the chromated and non-chromated systems, respectively. Clearly, these numbers indicate that the chromated system is more effective in protecting the underlying panel. Also, the behavior of the non-chromated coating system in the two environments was quite different. It should be noted that the 5 wt% NaCl solution used for the bulk immersion test is the makeup solution used in ASTM B117. The differences are that the B117 chamber creates a thin layer environment and the temperature is higher (35°C instead of room temperature). The plateau current for the immersed samples was approximately one-fifth that of salt spray exposed samples. Furthermore, there was less degradation detectable by visual inspection and OP analysis. After these initial results, immersion testing in 5 wt% NaCl solution was not pursued further.

In addition to galvanic current data obtained during exposure, OP was used to quantify the amount of material corroded and to gain insight on the attack morphology of each coating system. Figure 3 shows samples after exposure in B117 before removal of the coating. Large blisters formed around most fasteners in the sample with the non-chromated coating system. Interestingly, the one fastener that had no nearby blisters was heavily corroded itself as indicated by the orange coloration. This indicates that it was not interacting with the Al panel and received no galvanic protection. The other fasteners remained shiny.

In contrast to the non-chromated sample, the sample with the chromated coating system had no large blisters and appeared to be relatively unaffected. On the other hand, the measured galvanic current data in Figure 2 indicates that, even though the amount of current passed was less for the chromated coating system, it was still substantial in magnitude.

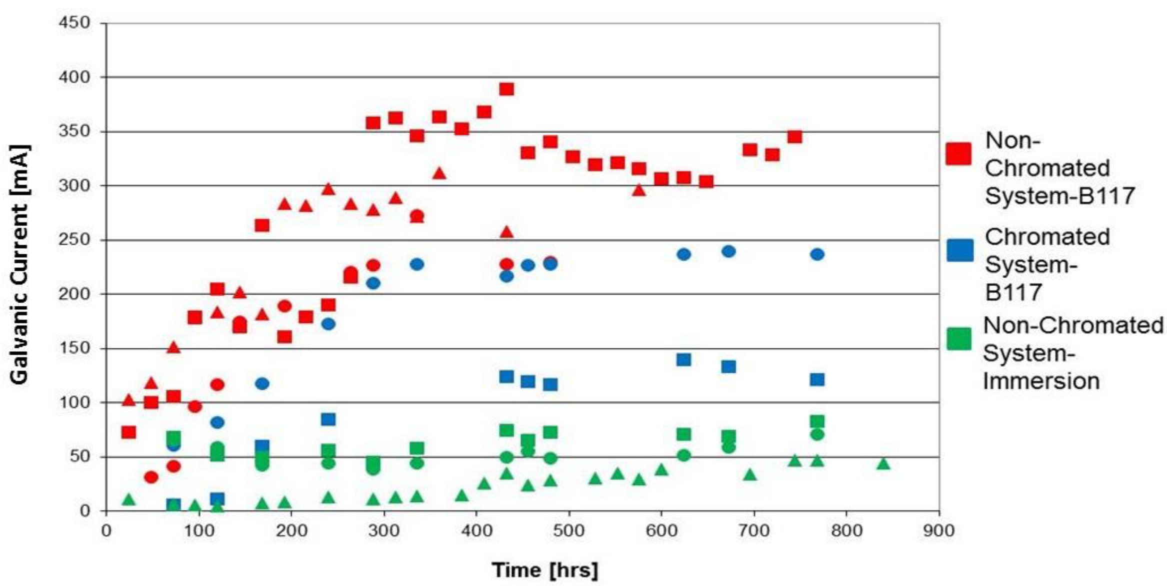


Figure 2: Compiled galvanic current data for replicated experiments with both coating systems exposed to ASTM B117 and for the non-chromated coating system immersed in 5 wt. % NaCl.

Figure 3: Photographs of non-chromated (left) and chromated (right) after 3 weeks exposure to salt spray fog.

After removal of the coating, it is clear that substantial attack occurred around one of the fasteners in the chromated system, Figure 4, even though it was not evident prior to coating removal. Furthermore, no attack was observed in the Al panel with the non-chromated coating at the one fastener that showed evidence of self-corrosion. The attack morphologies of the two coating systems can be compared. For both samples, attack was located close to the fasteners, not randomly dispersed across the sample area. However, the non-chromated system had widespread areas of attack that correlate well with the large blisters visible prior to coating removal, Figure 3. The attack also appears to be relatively uniform in nature in those areas. In contrast, the attack beneath the chromated system was limited to the region immediately surrounding, or underneath the one fastener. The attack was not widespread and uniform, but rather in the form of deep pits.

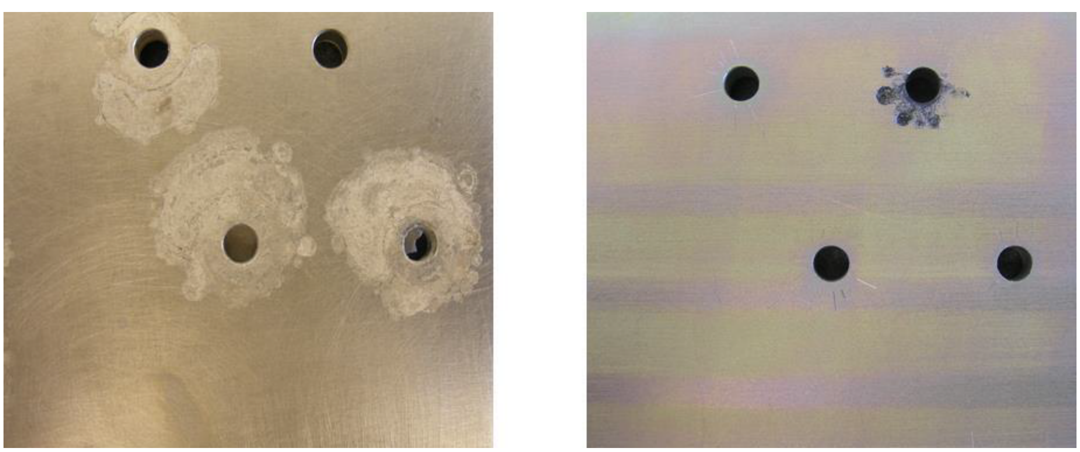
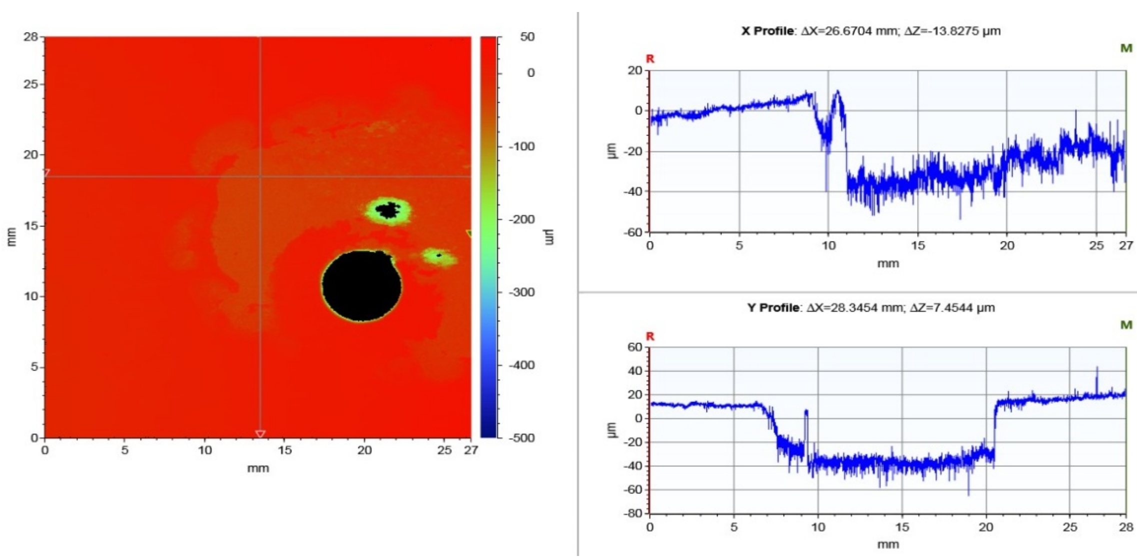


Figure 4: Photographs of samples from Fig 3 non-chromated (left) and chromated (right) after coating removal.

OP analysis, shown in Figure 5, can elucidate even more about the extent and type of corrosion. As discussed earlier, the non-chromated coating system exhibited very widespread attack that covered a large area around the fasteners. However this attack was relatively shallow, reaching a depth of approximately 50 μm, and was relatively uniform in the area previously under the blister. This differs greatly from the morphology seen in the samples with a chromated coating system where the attack was in the forms of deep pits, some of which reached depths of nearly 500 µm.

OP analysis can also be used to determine the total corroded volume of these samples. This corroded volume, along with the density of aluminum, can be used to calculate a mass loss, which can be compared to the equivalent mass loss calculated from the integrated current data. In general, the mass loss calculated from integration of the galvanic current data was lower than that calculated from OP data for the non-chromated coating system. For example, integration of the current measurement for the sample represented by the red squares in Figure 2 yields a mass loss of 0.065 g. However, the mass loss calculated from the missing volume determined by OP analysis was 0.074 g. The OP measured approximately 11% more attack than the amount predicted from the current measurements. It is possible that the average galvanic current was lower than the values determined from the intermittent ZRA measurements, i.e. the measured galvanic current was not representative of the actual current. However, another interpretation is that, in addition to the cathodic current on the fasteners measured as galvanic current, part of the cathodic reaction associated with dissolution occurred locally on the aluminum. Furthermore, in some cases severe crevice corrosion occurred at the interface of the sample and the epoxy mount resulting in attack on the sides and back of the sample. This volume (and associated mass) loss was not sensed by the OP analysis of the top surface. As a result, the measured galvanic current was a smaller fraction of the overall dissolution of the sample.



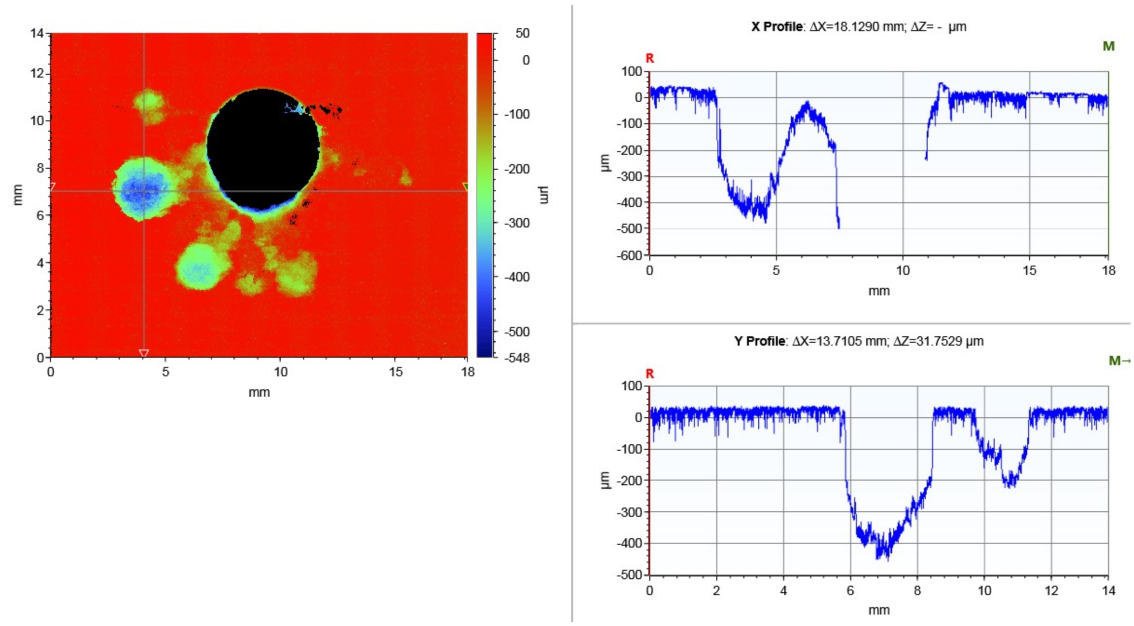


Figure 5: OP topographic maps (left) and line scans (right) of the region around a fastener in a non-chromated (top) and chromated (bottom) sample. The horizontal and vertical line scans are along the lines shown in the topographic maps. Note that the z scales in the topographic maps are identical to facilitate comparison. However, the contrast in the top left image of the non-chromated sample is not optimal as a result.

Larger discrepancies between the OP and galvanic current results were observed for the chromated coating system. In contrast to the non-chromate system, the equivalent mass losses from the OP data (0.0062 and 0.0064 g for the two chromated samples in Figure 2) were smaller than the mass losses calculated from the galvanic current (0.024 and 0.046 g, respectively). This difference could be associated with the fact that the OP is a "line of sight" method. The depth profiles in Figure 5 indicate that the pit walls of the chromated sample were quite vertical in nature. Any undercutting or attack beneath the edge of the pit at the surface cannot be detected by the OP. More work is required to clarify the reason for this disparity between OP and galvanic current measurements.

Figure 6 compares the results of this work with prior work, which used similar samples except that scribes were formed under two fasteners as shown in Figure 1. Differences were observed during the first 2 weeks of exposure in the salt spray environment. The presence of a scribe from the start of the experiment allowed immediate attack of the exposed metal surface. The galvanic current increased immediately and then decayed slowly as the corrosion sites developed. In contrast, samples with an intact coating (no scribe) exhibited an initiation period of approximately 10-14 days during which time the coating system broke down and the galvanic current slowly increased. It is quite interesting that the average galvanic current values measured after 2 weeks, which was enough time to reach steady state, were similar both with and without a scribe for samples coated with the non-chromated system.

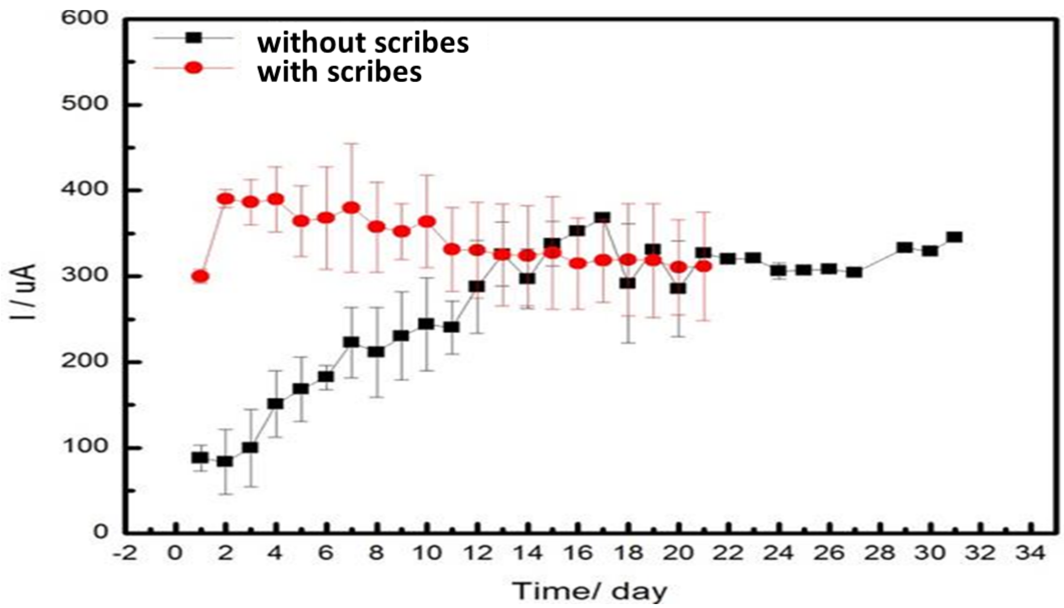


Figure 6: Galvanic current data for non-chromated coating system in salt spray conditions with (red circles) and without (black squares) scribes.

Impact of Fastener Hole Condition:

The work described above centered on determining the extent of degradation associated with the galvanic interactions between stainless steel fasteners and unscribed coated aluminum alloy panels in aggressive environments. The underlying assumption of this work is that attack was being initiated through defects intrinsic to the coating system. This study focuses on the initiation of corrosion attack in coated aluminum alloys, examining the possibility of extrinsic defects located within the fastener through-hole and beneath the fastener that might serve as initiation sites. Understanding the initiation of the degradation process could aid in more effective preventative measures to mitigate attack associated with galvanic interactions.

The impact of the condition of coating in the through-hole was examined to determine if extrinsic defects might be present prior to exposure. EIS was conducted on a variety of coating conditions to determine coating performance in each situation. Descriptions and illustrations of the various coating conditions are given below and illustrated in Figure 7.

- Away from Fastener – A coated portion of the sample not including the fastener in which no effects from the hole should be experienced.
- As Received – An area including the fastener and through-hole that has not been altered.
- Bare Hole – An area including the fastener and through-hole in which the coating within the hole has been mechanically abraded, exposing the bare aluminum alloy panel.
- Protected Hole – An area including the fastener and through-hole in which additional liquid epoxy coating has been applied between the fastener and the panel in order to provide additional barrier protection.

These experiments were carried out in a beaker containing 5 wt. % NaCl with a graphite counter electrode, saturated calomel reference electrode, and aluminum alloy panels coated with either non-chromated or chromate-containing coating systems as the working electrode. A SS316 fastener was inserted into the holes, but was not galvanically connected to the Al panel to mimic the geometry of the shorted samples. Samples were exposed to the sodium chloride solution for 12 hours before EIS was conducted to allow for uptake of solution into the coating. EIS measurements were made at OCP with a voltage signal of 10 mV over the frequency range from 10^5 to 10^{-3} Hz.

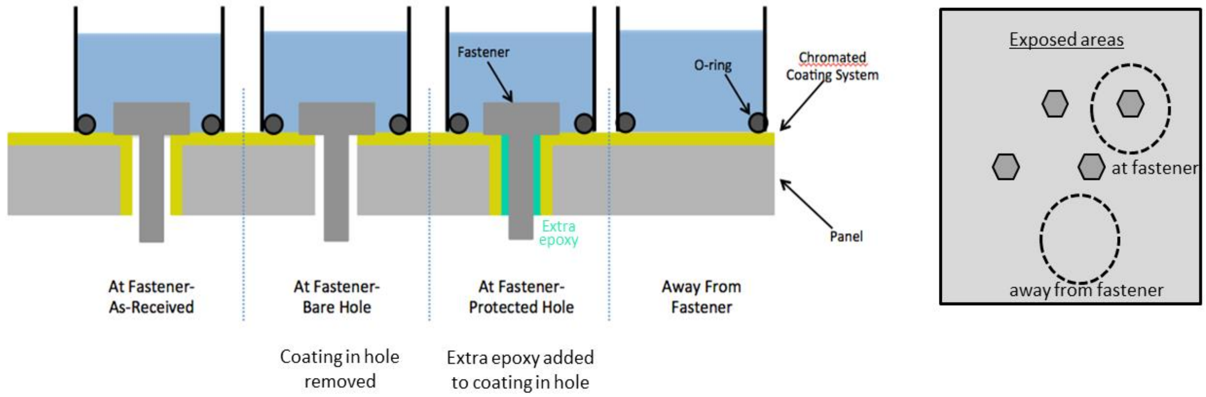
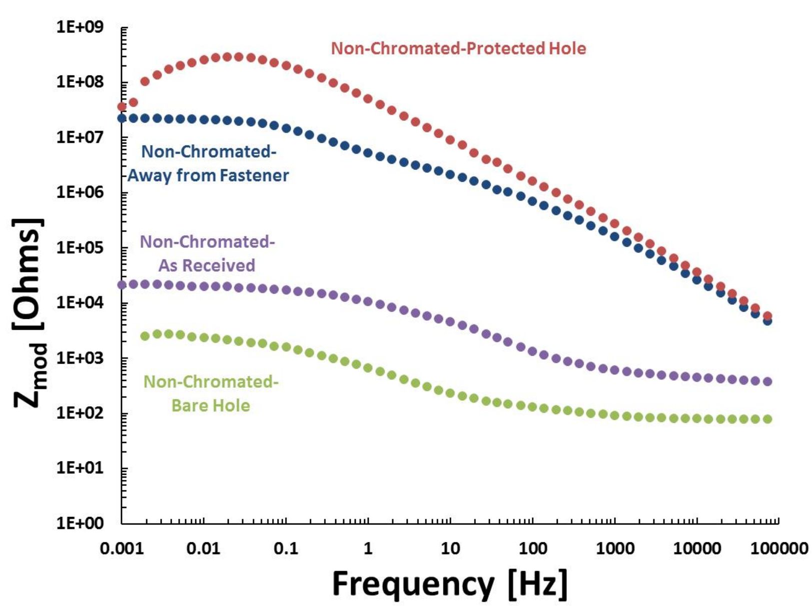


Figure 7: Illustration of each coating condition showing both a cross-section of the panel and the position of the exposed area on the panel. Note: Diagrams depict coatings with no extrinsic defects, which may not accurately illustrate coating within the hole.

Bode plots of the EIS spectra for the non-chromated coating system can be seen in Figure 8. The low frequency impedance measured around 1 mHz is representative of the resistance of the coated system to corrosion.



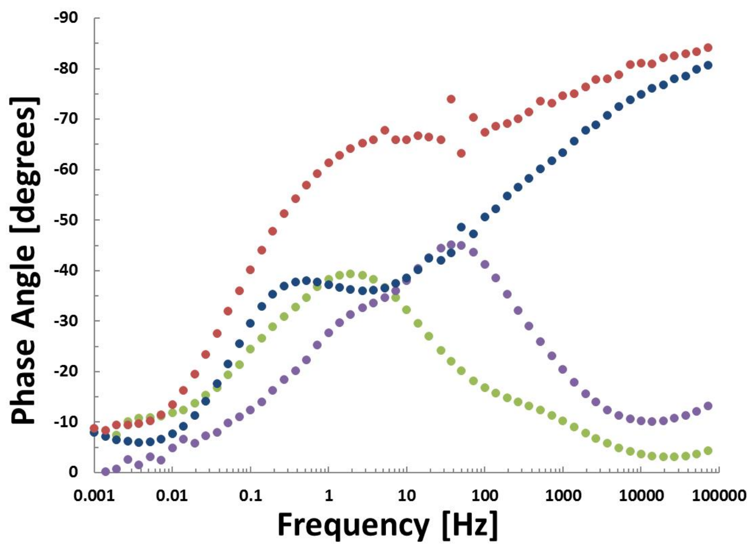


Figure 8: Bode plots, impedance magnitude (top) and phase angle (bottom) for non-chromated coating system.

The area away from the fastener can be assumed to contain no large-scale extrinsic defects, and have only defects intrinsic to the coating. Any large pores, for instance from lack of paint coverage at a contaminant particle, would have been immediately obvious but was never noticed for measurements made away from the fastener. Were the areas in or around the fastener hole free of any extrinsic defects, a low-frequency impedance similar to that away from the fastener would be expected. However, Figure 8 shows that the as-received condition has a low frequency impedance that is three orders of magnitude lower than that of the area away from the fastener. The low frequency impedance of the as-received condition is much closer to that of the bare hole, which is a worst-case condition in which the hole is left completely unprotected. However, when barrier protection is provided in the form of additional epoxy coating, the coating performance around the fastener is similar to that away from the fastener. While the as-received condition provided more protection in the hole than bare hole condition, it was not nearly as protective as the coating on the top surface of the panel. This is likely the result of defects and lack of coverage by the coating in the hole, resulting in inadequate protection of the underlying panel at the hole and providing initiation sites for corrosion attack.

Compared to the non-chromated coating system, the chromated system exhibited less of a decrease in coating performance near the fastener hole, Figure 9. Even though the organic coating within the hole did not fully cover the inner surface of the hole, similar to the non-chromated coating system discussed above, the chromate conversion coating provided much more protection than the PreKote adhesion promoter. Note that the CCC and PreKote pretreatments were applied by immersion in baths and therefore should coat the interior hole surfaces. The protection from the CCC resulted in significantly higher low frequency impedance compared to the non-chromated system in the as-received condition. However, the low-frequency impedance was still more than an order of magnitude lower for the as-received hole condition than for the control located away from the fasteners. These results confirm that defects in the fastener hole wall have a deleterious effect on coating performance even in the chromated case. Furthermore, it suggests that during prolonged exposure to an aggressive environment, corrosion attack is likely to initiate first at these defect sites, and not through degradation of non-defective coating regions.

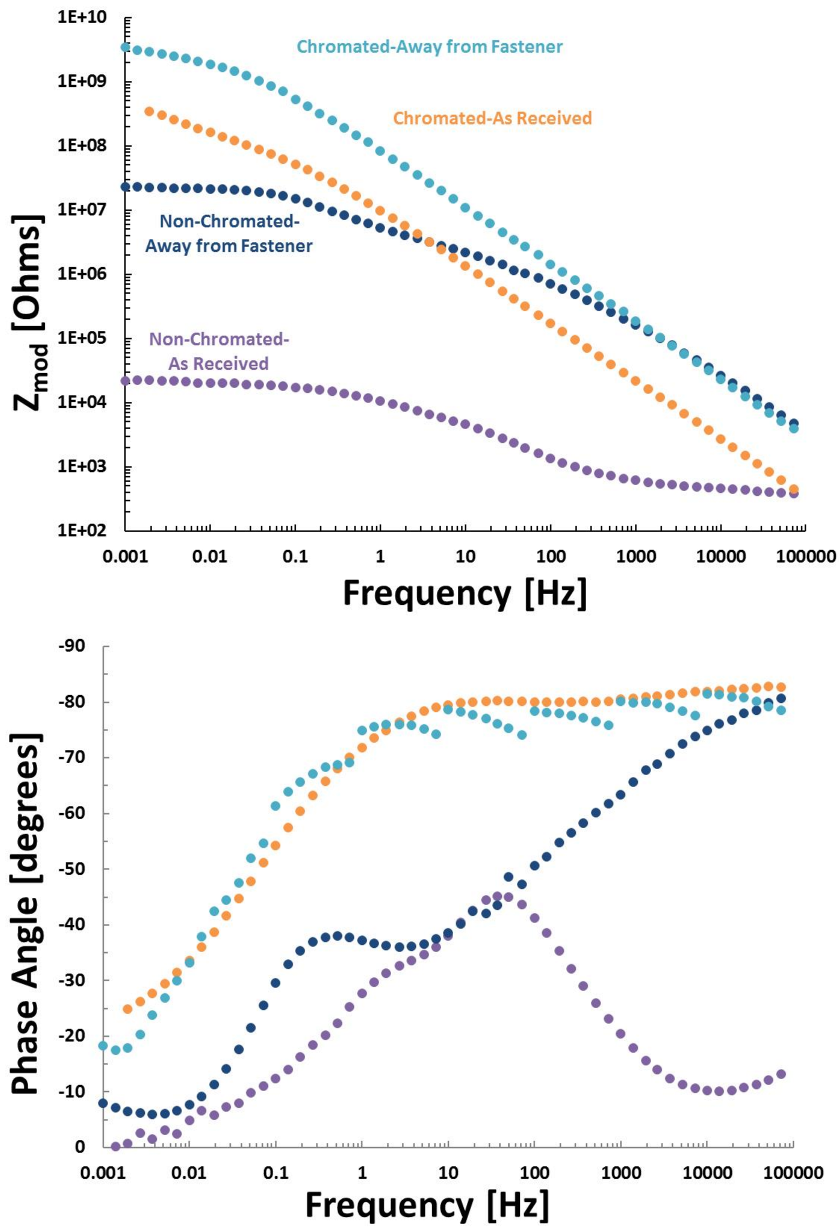


Figure 9: Bode plots, impedance magnitude (top) and phase angle (bottom), for each hole condition for the chromated coating system.

Based on these results, it can be inferred that applying additional protection to the hole, for instance between the fastener and panel during assembly, would significantly improve resistance to galvanic corrosion in corrosive conditions. To test this, a sample was constructed using the protected hole geometry shown in Figure 7 but on a complete 4-hole panel with an unscribed non-chromated coating system. The SS316 fasteners were shorted to the panel during exposure to ASTM B117 salt spray, and the measured galvanic current is shown in Figure 10. For comparison, the current measured for the unscribed as-received coating, which was shown in Figure 2, is replicated on the right of Figure 10.

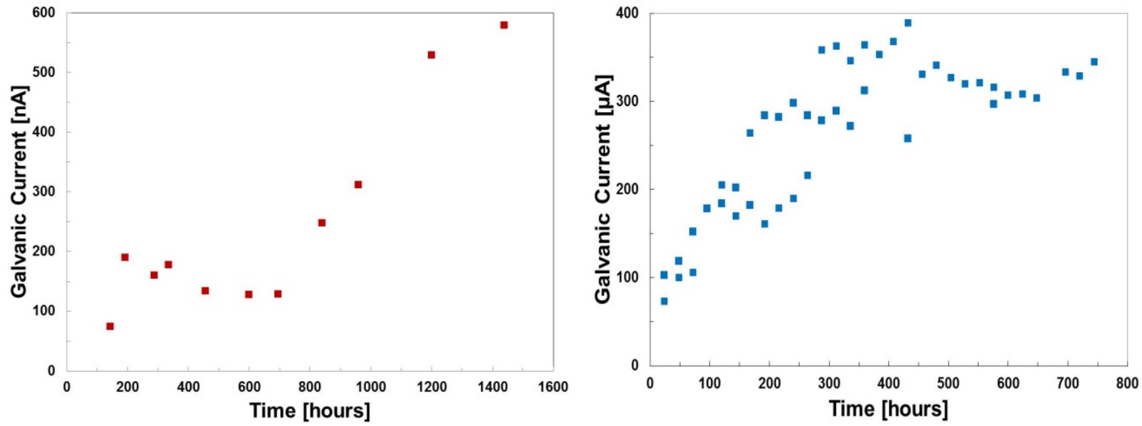


Figure 10: Galvanic current measured as a function of exposure time in ASTM B117 for as received galvanic panel (right, replicated tests) and galvanic panel with additional epoxy coating (left). Note the different units for galvanic current on the y-axis and the different exposure time for each condition.

The galvanic current for the as received condition increased linearly with time for the first 300 h of exposure, then became time-independent at a value between 300 and 350 µA. In contrast, the additional barrier protection between the panel and fastener dramatically decreased the measured galvanic current. The galvanic current remained between 100-200 nA for approximately 700 h and then began to increase, apparently signaling the initiation of a defect, and reaching about 600 nA after 1500 h. Taking note the difference in units, this galvanic current is about three orders of magnitude lower than for the as-received condition. As shown in Figure 11, this experiment was continued for 180 days. After about 1500 days or 2 months, the galvanic current began to increase significantly, suggesting that the defect grew to a macroscopic condition. Even after 180 days, the measured current for the sample with added protection was still less than 100 µA, whereas the current for the as-received condition started at 100 µA and reached 300 µA after about 14 days of exposure to B117 salt spray. This indicates that breakdown of the coating can eventually lead to galvanic attack of the underlying panel even when the hole contains extra protection. However, this degradation takes a much longer time to initiate and grow.

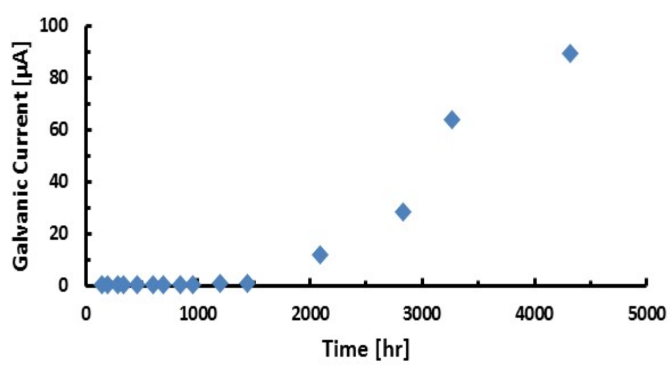


Figure 11: Measured galvanic current for galvanic panel with additional liquid epoxy coating protecting defects within fastener hole.

The condition of the panel after exposure, as shown in Figure 12, is also of interest. Attack is only evident at one fastener site, and the attack is relatively confined. Recall the as-received, unscribed, non-chromate coating without extra protection in the fastener hole area exhibited massive blisters surrounding most or all of the fasteners.

Figure 12: Image of galvanic panel with protected fastener holes after 180 days exposure to salt spray conditions.

In addition, all of the fasteners themselves have experienced self-corrosion. The significance of this is that the stainless steel fasteners, which are noble to the panel, should be protected by galvanic coupling if such an interaction is taking place. The attack of the fasteners is indicative of the lack of current flowing from fastener to panel due to the additional protection afforded to potential initiation sites within the hole.

It is apparent that the protection provided near the fastener on as-received samples is inadequate and not on par with that away from this region, highlighting the importance of through-hole preparation in real applications. Actions during coating deposition or preparation of the galvanic panels can compromise the protection of the coating in the fastener hole region. Visual inspection of as-received through-hole wall surfaces indicated that the coating is somewhat thin in areas, which could potentially serve as initiation sites for attack. In addition, assembly of the panels, in particular the friction between a washer and top coat during fastener assembly, could damage the coating beneath the fastener and result in creation of initiation sites.

Impressed Current:

An impressed anodic current approach was also used to examine sites susceptible to corrosion attack. The experiments described above relied on current provided through galvanic interaction between the panel and more-noble SS316 fasteners to drive aluminum dissolution. This galvanic current varied with time and was measured periodically with a ZRA. It could be integrated with respect to exposure time to determine a total charge passed through galvanic interaction. The impressed current approach is a more controlled means of delivering this charge by fixing the current between the panel and a counter electrode. This current can be transferred to the panel through intrinsic or extrinsic defects to complete the circuit. The current can be set to any value, and so can be larger than the natural galvanic current. Larger currents allow for the same charge to be passed in a shorter time, thus accelerating the testing and providing faster feedback. As with any accelerated test, it is of course important not to change the mechanism of degradation. Fasteners are not required in this method, meaning that susceptible areas of the panel will be attacked independent of their proximity to the fastener sites. An illustration of this experimental setup is shown in Figure 13.

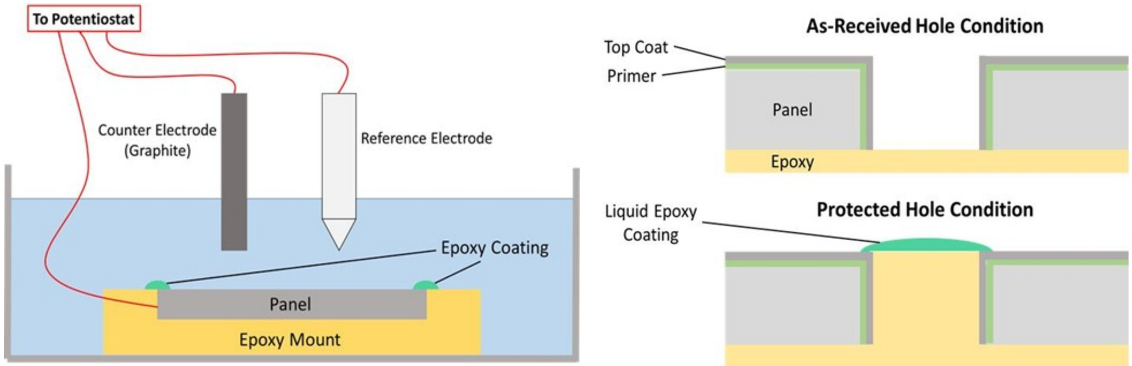


Figure 13: Experimental setup (left) and the hole conditions (right) used in impressed current experiments.

The panel was embedded in epoxy to expose only the top surface of the panel. Additional liquid epoxy coating (shown in green) was used to protect the interface of the panel and epoxy from crevice attack. In this study, two hole conditions were analyzed. The first is an as-received condition in which the epoxy was not permitted to fill the fastener hole, so that the hole wall was exposed. The second setup allowed the epoxy to fill the hole, preventing attack within the hole. Again, liquid epoxy was applied to the top to protect the interface. The purpose of these conditions was to isolate the effect of defects in the fastener hole.

Current was then passed for an amount of time that would yield a charge equal to that calculated for exposure of a galvanic panel to salt spray conditions for three weeks. The results are shown in Figure 14 for an experiment with an applied current of 10 mA.

For the protected hole condition, the circuit was not completed, resulting in a measured potential of many volts, essentially reaching the compliance of the potentiostat. Furthermore, the measured current was extremely low, on the order of 0.02 mA, even though the potentiostat tried to apply 10 mA. Finally, no attack was observed on the sample at the end of the test after the coating was removed. In the case of the as-received hole, a reasonable potential of about -0.4 V SCE was measured that was indicative of active aluminum dissolution. The measured current was equal to the applied current of 10 mA for the duration of the exposure, and significant attack occurred to the hole wall, Figure 15.

No attack was observed on the top of the panel for either condition, but a large volume of material was removed in localized areas within the hole for the as-received hole condition, likely corresponding to areas of poor coating coverage. This technique was also attempted in salt spray conditions. For this experiment, fasteners were used and served as the counter electrodes through which current was passed from the potentiostat. The holes were in the as received condition. A period of 24 hours of exposure was used prior to starting the impressed current to allow water uptake into the coating and the formation of an electrolyte layer on the surface. Results are shown in Figures 16 and 17.

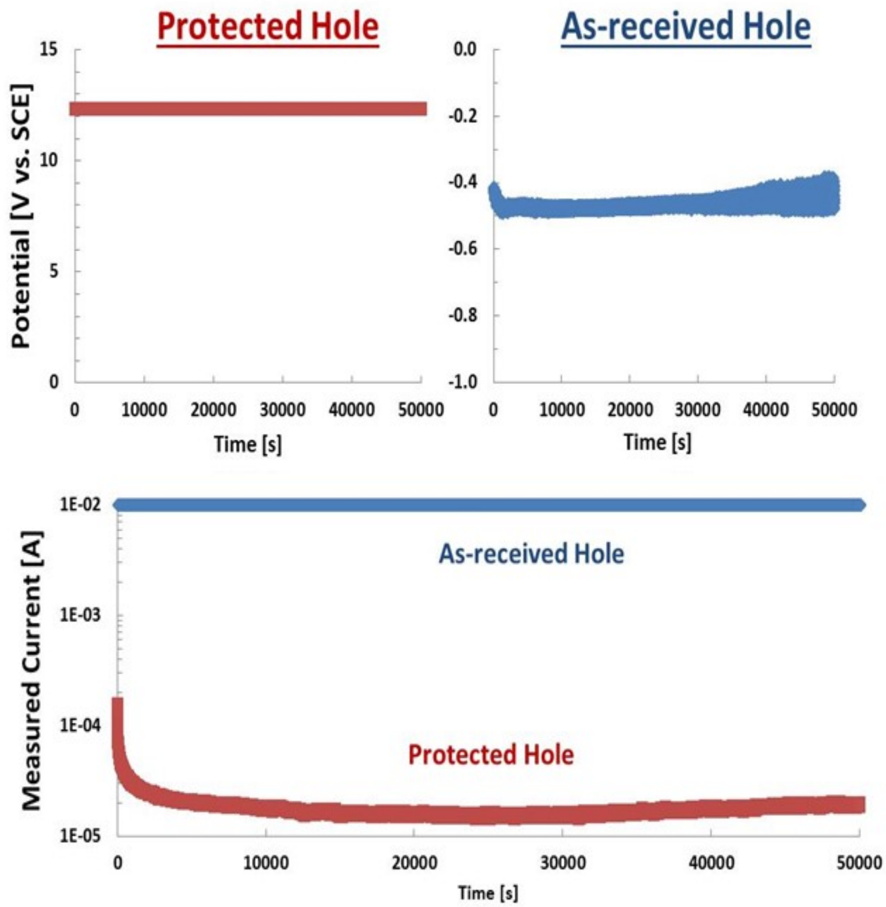


Figure 14: Measured potential (top) and current (bottom) for as-received and protected hole conditions. Note the difference in scale of the y-axis for the potential plots.

Figure 15: Images of sample with as-received hole condition after impressed current testing, showing damage induced to fastener hole wall during impressed current and no attack on top surface (left).

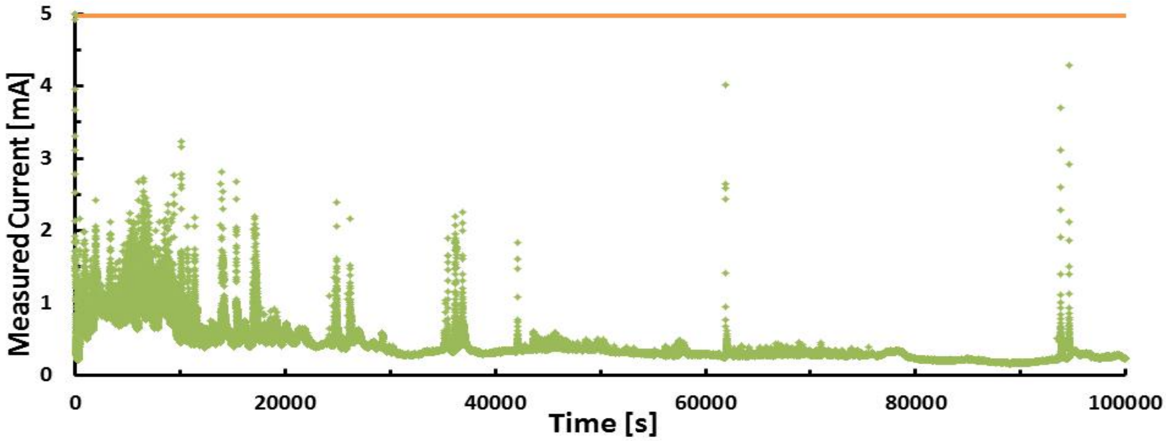


Figure 16: Applied current (orange) and measured current (green) for impressed current experiment in salt spray conditions.

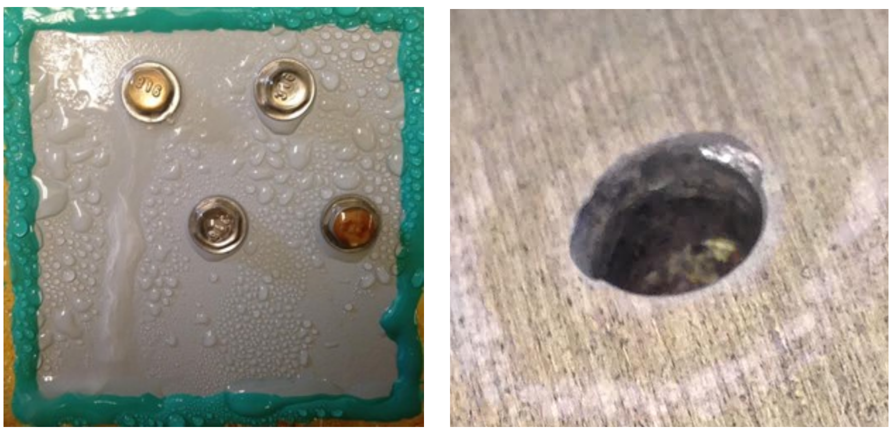


Figure 17: Images of the assembled panel (left) and hole (right) after impressed current experiment in salt spray conditions.

As can be observed in Figure 16, the measured current was a fraction of the applied current of 5 mA, with only 32 of the 500 C of charge passed between the fasteners and panel. The condition of the fasteners indicated that current did not flow evenly to all four fasteners. The presence of rust on the top-left and bottom-right fasteners indicate that these fasteners were not protected by cathodic current even though they were also electrically connected to the other fasteners. Current apparently flowed only to fasteners in close proximity to coating defects in the holes. It is also noteworthy that no blisters or other coating degradation typically associated with salt spray exposure were evident. This suggests that attack occurred at preexisting defect sites. This is evident in Figure 17, showing that the attack was similar to that for the impressed current testing during immersion.

<u>Conclusions:</u>

This work has clarified and quantified a few distinct characteristics of the degradation of chromated and non-chromated coating systems on aluminum alloy panels as driven by galvanic interaction with more-noble SS316 fasteners. The galvanic current data show that the galvanic current for panels coated with a non-chromated system is appreciably higher than that of chromated coating systems. The galvanic driving force, i.e. the current emanating from the uncoated fasteners, was the same for the two systems. However, the chromated system effectively reduced the total amount of material lost under these aggressive conditions. While this metric indicates that the chromated system is better, differences in the attack morphology must also be considered, as the two coating systems induce vastly different corrosion morphologies in the underlying aluminum alloy substrate. The non-chromated system experienced more widespread attack with more material lost to degradation, but the attack was limited to around 50 nm in depth and is relatively uniform in nature. The chromated system exhibited very localized corrosion with less mass lost, but the pits exceeded 400 μm in depth. In addition, this attack was located close to the fastener hole, and sometimes even damaged the hole wall itself. This corrosion morphology could prove to be much more detrimental to the integrity of a part than that exhibited by panels with non-chromated coatings, despite the lesser amount of total attack. It should also be noted that the ease of detection of the degradation for each coating type varied drastically. Visual inspection of a corroded part with the non-chromated system could detect the occurrence of degradation from the blisters formed as a result of coating delamination. However, detection of degradation occurring on a part with a chromated coating system would require a more advanced method to sense loss under the coating.

The work focused on determining how attack initiates on unscribed coated panels with through-holes and fasteners. It has been determined that the performance of the coating in close proximity to the fastener holes is not equal to that away from the fasteners. Comparison of these two regions shows that, unlike the area away from the fastener, the coating in and near the hole is largely ineffective at preventing corrosion attack. Impressed current experiments show that attack cannot be initiated at an area of coating free from extrinsic defects in the time frame studied, but extensive damage occurs when the fastener hole wall is exposed to the same conditions. Extrinsic coating defects do exist in the fastener hole wall, and these defects are potential sites for initiation of galvanic attack. This point is further supported by the dramatic decrease in galvanic current measured when simple barrier protection is utilized between the fastener and panel. Even with double the exposure time to very aggressive salt spray fog conditions, galvanic current was three orders of magnitude lower than that measured for the as-received panels. Not only are these defects present, but their location is also troubling. Because the potential initiation sites are located in the fastener hole wall, they are located very close to the cathode with a very large cathode to anode area ratio, which further intensifies attack once it initiates.

It has also been shown that impressed current is a viable accelerated corrosion method in immersion environments. However, even impressed current will not accelerate attack without the effect of coating defects in and near the fastener hole region. Attack will only occur in the presence of preexisting initiation sites for the exposure times studied. Impressed current in salt spray conditions was possible but much less effective. The attack that did occur correlated with impressed current experiments in immersed conditions.

Insight gained from these studies can be leveraged to develop a tool that encompasses the critical parameters and provides predictions of the galvanic coupling susceptibility, as is planned for the follow-on program funded by ONR. The impressed current method will be incorporated into this work with a couple of changes. First, the environment will consist of cyclic salt spray exposure tests, not bulk solution. In addition, an artificial defect, or scribe, will be used to control the defect condition of the coating. Lastly, the test panel will be simplified to contain only one fastener and fastener hole. The proposed work will systematically address the environmental factors influencing corrosion behavior in a way that can guide both component designers and developers of predictive software programs, and also provide data that can be used for verification of those predictive models. Proposed work will focus on the development of damage functions that depend on environmental factors and time. The damage functions might be defined as the volume of lost material as a function of time, the volume of lost material divided by the area of attack, which is just a nominal depth of attack, or just the area of attack since the attack volume is cathodically controlled. These factors can be determined by optical profilometry.

Plans and Recommendations for Future Work:

Insight gained from these studies can be leveraged to develop a tool that encompasses the critical parameters and provides predictions of the galvanic coupling susceptibility, as is planned for the follow-on program funded by ONR. The impressed current method will be incorporated into this work with a couple of changes. First, the environment will consist of cyclic salt spray exposure tests, not bulk solution. In addition, an artificial defect, or scribe, will be used to control the defect condition of the coating. Lastly, the test panel will be simplified to contain only one fastener and fastener hole. The proposed work will systematically address the environmental factors influencing corrosion behavior in a way that can guide both component designers and developers of predictive software programs, and also provide data that can be used for verification of those predictive models. Proposed work will focus on the development of damage functions that depend on environmental factors and time. The damage functions might be defined as the volume of lost material as a function of time, the volume of lost material divided by the area of attack, which is just a nominal depth of attack, or just the area of attack since the attack volume is cathodically controlled. These factors can be determined by optical profilometry.

Metrics:

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Poster Presentations by J. Boerstler:

NACE 2016 Student Poster Session, Vancouver, BC, March 4-11, 2016, "*Corrosion Degradation of Coated Aluminum Alloy Systems Through Galvanic Interactions*"

Gordon Research Conference and Symposium, Colby Sawyer College, NH, July 9-15, 2016, "*Corrosion Degradation of Coated Aluminum Alloy Systems Through Galvanic Interactions*"

NACE 2017 Student Poster Session, New Orleans, LA, March 26-31, 2017, "*Corrosion Degradation of Coated Aluminum Alloy Systems Through Galvanic Interactions*"

Oral Presentation by J. Boerstler:

232nd Electrochemical Society Meeting, Light Alloys Symposium, National Harbor, MD, October 3, 2017, "*Accelerated Corrosion Degradation of Coated Aluminum Alloy Systems through Galvanic Interactions*"